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BEHAVIOR OF CONCRETE EXPOSED TO THE SEA

by

Bryant Mather

January 1970

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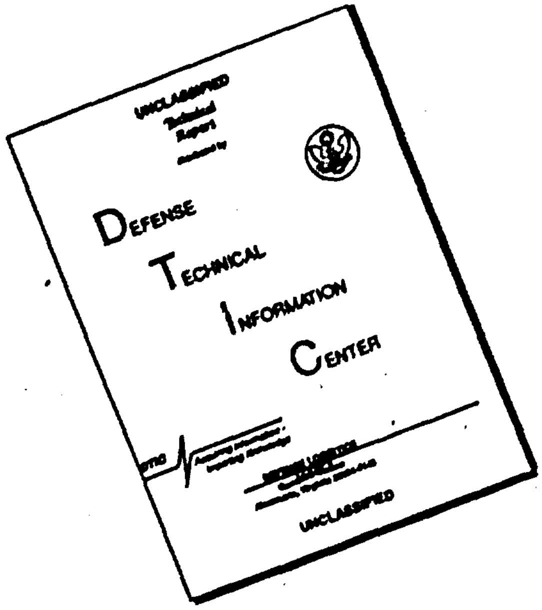

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(10) Bryant Mather

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FOREWORD

Under date of 24 December 1968, the Chief of Engineers informed the Director, Waterways Experiment Station (WES), that it was desired that representatives of the WES prepare a paper on any appropriate ocean engineering subject to be offered for inclusion on the program for the Conference on "Civil Engineering in the Oceans, II" to be held in Miami Beach, Florida, 10-12 December 1969, under the sponsorship of the Council on Ocean Engineering of the American Society of Civil Engineers. In accordance with this request, an abstract was prepared and forwarded to the program chairman for his consideration. Under date of 7 May 1969, advice was received that the paper on "Behavior of Concrete Exposed to the Sea" had been accepted. The paper was presented as the second paper in the Materials Session of the Conference, on 12 December 1969. Copies have been furnished to the ASCE Technical Publications Department for inclusion in the proceedings of the conference. Copies were also furnished for review and approval to the Office, Chief of Engineers, and the paper was cleared for presentation and publication.

The paper is a summarization of relevant aspects of the state of knowledge in relevant areas.

COL Levi A. Brown was Director of the WES during the preparation of this paper and Mr. F. R. Brown was Technical Director.

BEHAVIOR OF CONCRETE EXPOSED TO THE SEA*

by

Bryant Mather**

INTRODUCTION

Hydraulic-cement concrete has been employed in the construction of works exposed to the sea since the Roman Empire. The first reinforced concrete structure made using portland cement is still in service. In spite of this long history of successful use, there are still instances of concrete that undergoes severe deterioration and destruction when exposed to the sea that would have served satisfactorily in a nonmarine environment.

Research on the factors affecting durability of concrete in marine exposures has been conducted at many laboratories and has yielded a body of data that is satisfactory to permit practical measures to minimize the likelihood of damage in most instances. Further work is needed to fully elucidate the interacting roles of various constituents of cement with the chloride and sulfate ions of sea water. Additional research is also needed to fully appreciate the several mechanisms that may accelerate the corrosion of ferrous metal embedded in concrete exposed to the sea. The use of portland cements containing less than 8 percent tricalcium aluminate as calculated from the chemical analysis will normally prevent deleterious sulfate attack. However, there are distinct indications that cements with calculated tricalcium aluminate contents approaching zero are in some respects less desirable than those in the intermediate range between zero and 8 percent. It is indicated that the benefits of having some tricalcium aluminate present are related to the tendency of this component to combine also with chlorides and thus reduce the rate at which chloride ions may become available at the interface with reinforcing steel to promote corrosion. Further research is ~~also~~ needed to interrelate the physical parameters of pore structure as these control permeability and strength with the chemical parameters. that control the nature, amount, and rate of formation of products of increased volume that generate internal expansion. ?

*Prepared for presentation at the Conference on "Civil Engineering in the Oceans, II," Miami Beach, Florida, 10-12 December 1969, under the sponsorship of the Council on Ocean Engineering of the American Society of Civil Engineers.

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*for minimizing sea water deterioration of concrete.

In Beach Erosion Board Technical Memorandum No. 96, published in 1957, a discussion was presented of the "Factors Affecting Durability of Concrete in Shore Structures" (Mather, 1957). In 1969 the Proceedings of the RILEM International Symposium on Durability of Concrete were published (RILEM, 1969) covering "Basic Questions, Principles and Methods of Testing and Determination of Concrete Durability under the Action of Frost, Sulfates, and Acids; and Corrosion of Reinforcement and Its Prevention." Prior to 1957, between 1957 and 1969, and in the future, these matters have been and will be under further study throughout the world. When concrete does not behave satisfactorily as a result of exposure to the sea the cause is, as is the case in all instances of unsatisfactory performance, that the appropriate levels of quality were not obtained. The failure to obtain these levels of quality results either from failure to require them in specifications or failure in the execution of the work to comply with the specified requirements. Hence, the obtaining of satisfactory performance depends upon: (a) an assessment of the performance requirements, (b) an evaluation of the environmental influences, (c) an understanding of the results of research on the interrelation of environmental influences, quality levels, and achieved performance, (d) selection and specification of relevant quality levels, and (e) insuring compliance with specified requirements.

DETERIORATION-PRODUCING PHENOMENA

Many phenomena that contribute to the deterioration of concrete do so by mechanisms that induce internal expansion. That which expands may be a constituent of the cement, a constituent of the aggregate, or the contents of a pore or void in the concrete. These phenomena include: frost action, alkali-aggregate reaction, sulfate attack, and a variety of chemical reactions not involving alkalies or sulfates. Similarly, deterioration may be induced by nonuniform contraction. Phenomena inducing such contraction include drying and carbonation. Deterioration of concrete may occur due to solution and removal by leaching of the soluble constituents of the cement paste in the concrete. Deterioration of concrete may also occur as a secondary consequence of structural overloading that results from the interaction of external mechanical forces, such as those induced by foundation movements, seismic forces, and explosions. When concrete is found to have deteriorated following the occurrence of such abnormal loadings of the structure in which the concrete was used, it is assumed that the deterioration is a secondary consequence of the structural failure that preceded or accompanied the deterioration. Such deterioration can be avoided only by structural design to resist the imposed loads. Cracking which occurs due to uncontrolled termperature variations in a structure does not of itself cause deterioration in the sense of this discussion, but it does increase the vulnerability to deterioration due to frost action or sulfate attack.

PERTINENT FACTORS IN A SEAWATER EXPOSURE

Concrete exposed to seawater will be subjected to wetting by an aqueous solution containing principally dissolved sodium chloride and magnesium sulfate. The oceans contain, on the average, about 35 parts per thousand (3.5 percent) dissolved salts. The major cations, Ca^{++}, Mg^{++}, Na^{+}, and K^{+}, exist in seawater largely as uncomplexed species.

The major anions include Cl^-, which is also not strongly complexed, and CO_3^-, HCO_3^-, and SO_4^-, which are. Expressed as milligrams per liter of seawater, the principal elements present in solution are chlorine, 19,000; sodium, 10,600; magnesium, 1,300; sulfur, 900; calcium, 400; and potassium, 380. All other elements are probably present, but no others make up more than 65 mg/l. The six elements mentioned make up 99 percent of the dissolved salts in seawater. Although the concentration of dissolved solids has been found to vary from place to place, the ratio of any one of the major constituents to the total dissolved solids is nearly constant everywhere (ACS, 1964).

Thus, the factors inherent in seawater exposure that should be considered for their effects on concrete are freezing and thawing, wetting and drying, and chemical reaction of chlorides, sulfates, alkalies (sodium and potassium), and, in some instances, dissolved carbon dioxide.

The elements of concrete that may be affected by wetting or by chemical reaction with chlorides, sulfates, or alkalies include the cement, the aggregates, and reinforcing steel or other metal, if present.

EFFECTS OF CONTINUOUS IMMERSION OF CONCRETE IN SEAWATER

Concrete that is totally and continuously immersed in water, even if the water contains dissolved salts such as are found in seawater, generally may be regarded as being in a protected exposure. Continuous immersion usually provides a uniformity of environment with respect to temperature and moisture content that prevents the immersed concrete from being subjected to such deteriorating influences as frost action, volume change due to wetting and drying, and differential volume change due to moisture content differences between the surface and the interior. Continuous immersion also tends to reduce the potential for chemical reaction by removing changes in the degree of saturation as a mechanism for the flow into and out of the concrete of solutions containing ions capable of attacking constituents of the concrete, and leaving only concentration gradients as the means of ingress of such ions. Locher and Pisters (1964) note that, under equal conditions of exposure, the aggressiveness of water increases with increasing concentration of the relevant substances, but that aggressiveness is also increased by higher temperatures, higher pressures, wetting and drying, or mechanical abrasion by fast-flowing or turbulent waters.

EFFECTS OF INTERMITTENT IMMERSION OF CONCRETE IN SEAWATER

Most concrete structures exposed to seawater are partially or wholly situated so that they are sometimes immersed in seawater and sometimes exposed to the air. If the structure is located where the temperatures fall below freezing, the concrete exposed to the air with falling tide is probably subjected to as severe frost action as is any concrete in natural exposure. The realization that concrete exposed in the tidal zone in a region of low winter temperatures would be subjected to very severe frost action resulted in the selection of the mean-tide elevation at Treat Island, Cobscook Bay, Me., as the location for the U. S. Army Corps of Engineers severe natural weathering station. This location has been used since 1936

by the Corps of Engineers to develop information rapidly on the relative resistance of concretes to frost action (Kennedy and Mather, 1953).

The second important effect on concrete related to wetting and drying is the volume change relations due to changes in, or changes in uniformity of, moisture content. These phenomena are often referred to as drying shrinkage effects.

In localities such as Treat Island, the mean temperature of the seawater is low and chemical reactions take place relatively slowly. Concretes relatively deficient in resistance to frost action seldom survive long enough to manifest any readily observable effects of chemical attack; hence, it can be argued that there is a general tendency for the severity of chemical attack to be reduced when that of physical attack increases, and vice versa.

CHEMICAL ATTACK OF SEAWATER ON CONCRETE

The potentially aggressive constituents of seawater with respect to concrete are the sulfate, chloride, carbonate, bicarbonate, alkali metal, and magnesium ions. Since in seawater the sulfate component is magnesium sulfate rather than sodium or calcium sulfate, as is more often the case in sulfate-attack situations not involving seawater, the various chemical reactions of magnesium sulfate with several of the constituents of hydrated portland cement are somewhat different. F. M. Lea (1956) pointed out that, initially, magnesium sulfate has a similar action to that of other sulfates in attacking calcium aluminate hydrate, but that later it can induce a significantly different and more far-reaching effect because of its ability--as distinguished from other sulfates--to attack and decompose the calcium silicate hydrate. This reaction proceeds to completion because of the low solubility of magnesium hydroxide.

The carbonate and bicarbonate ions may participate in the reaction of carbonation of calcium ion or calcium hydroxide formed during hydration of cement. In a discussion of deterioration of concrete in the shipways at Newport News, Va., Mrs. Terzaghi (1948) concluded that two processes were at work, one involving sulfate attack that caused internal expansion and cracking, and the other involving carbon dioxide dissolved in the water as carbonic acid that caused local softening and disintegration. The water samples taken from relief wells in these shipways were regarded as containing from 30 to 60 percent seawater, based on chloride content, and had free CO_2 contents of 7 to 99 mg/l; the highest CO_2 content was found in the sample of lowest seawater content which had 57 mg/l aggressive CO_2 and a pH of 6.9.

Internal contraction due to carbonation has been found to occur at the maximum rate and to the greatest extent when the concrete is subjected to an environment in which the relative humidity is close to 50 percent. Carbonation, like drying, is a phenomenon that proceeds from the surface inward and consequently the degree to which a given concrete element is affected over a given period of time decreases markedly with decrease of surface:mass ratio. Carlson (1937) has shown that an occasional wetting of a concrete surface will prevent drying to a considerable depth because

dry concrete will absorb as much moisture in one day as wet concrete loses in two weeks of drying. It is therefore concluded that drying shrinkage and carbonation shrinkage are unlikely to be major sources of deterioration of concrete in the ocean. Apparent confirmation of this conclusion is suggested by the virtual absence of reports of such deterioration in the available literature. It is suggested that concrete deterioration in seawater due to these causes is largely precluded by the typical nature of the environment, the typically low surface:mass ratio of the structural elements involved, and the avoidance of materials, proportions, and construction practices that would be conducive to development of this sort of deterioration, as these are avoided for other reasons.

Alkalies

The alkali metal ions may participate in any of several reactions with reactive silica or reactive carbonate constituents of the aggregates. Stanton (1937) listed among structures adversely affected by alkali-silica reaction, sections of seawalls in Ventura and Santa Barbara Counties in California. As far as is known, there have as yet been no documented cases of alkali-carbonate reaction which have caused deterioration of concrete structures exposed to seawater. Kennedy and Mather (1953) found that in concrete containing a crushed limestone aggregate that had been exposed to seawater at Treat Island, there was evidence of the formation of reaction rims on certain limestone coarse-aggregate particles. The particular limestone studied contained about 4 percent of a montmorillonitic clay which undergoes greater swelling when wetted with a solution containing sodium ion than when sodium ion is not present. They showed that this material, processed as manufactured fine aggregate, exhibited two to three times as much increase in volume when immersed in seawater as when immersed in fresh water or in a saturated solution of calcium hydroxide. Buck and Mather (1969) described an instance, believed to be the first of record, of deterioration of concrete due to alkali-silica reaction in which the reactive aggregate was quartz. Since the affected structure was a dry dock at Charleston, S. C., it was first assumed that the unusualness of the reaction might have been due to the involvement of seawater. However, the reaction product was principally a potassium silicate rather than a sodium silicate which indicates that alkalies from the seawater were not significantly involved. It was concluded that the unusualness was related to the physical rather than the chemical aspects of the environment.

Expansion of concrete caused by the swelling of the alkali-silica gel formed in concrete by the reaction of alkali and soluble silica can normally be prevented in any of three ways. It can be prevented by the avoidance of the use of aggregate materials containing soluble silica; or it can be prevented by the restriction on the composition of the portland cement with respect to alkali content so that the total amount of sodium oxide and potassium oxide, calculated as sodium oxide, does not exceed 0.60 percent; or finally, it can be prevented by the use in the concrete of adequate amounts of finely divided active silica introduced in the form of pozzolan. So far as is known, there has been no deterioration of concrete due to alkali-silica reaction in concrete in which any of the three preventive measures have been employed. Informal reports are rather frequently encountered that purport to refer to such deterioration in concrete made with low-alkali cement. In all of these

cases that have been adequately examined, it has been found that the cement that was intended to be low alkali was in fact not low alkali, or that some abnormal condition of exposure arose in which the alkali from a technically low-alkali cement was presumably so concentrated during exposure as to render the chemical environment of the aggregate similar to that which would have been produced in a more normal environment had a high-alkali cement been used. From these considerations it therefore follows that if for reasons of economy, workability, and reduction in heat evolution there are benefits to be obtained by the use of substantial quantities of chemically active pozzolans whereby relatively large quantities of finely divided soluble silica are incorporated in the concrete, this practice will be beneficial in preventing deterioration due to the alkali-silica reaction.

Chlorides

The chloride ion may participate either in chemical reactions similar to those involving the sulfate ion--so as to yield such products as chloraluminates that are analogous to sulfoaluminates--or in reactions involving the corrosion of reinforcing or other embedded metal. In this latter connection, Halstead and Woodworth (1955) reported that reinforced concrete structures exposed under coastal conditions (within 10 mi of the seacoast) in South Africa have, in some cases, shown deterioration believed caused by electrochemical corrosion of the steel. In the discussion of their paper, it was noted that the South African Railway Administration has adopted the policy of using reinforced concrete structures in preference to steel because of difficulties in maintaining steel structures. This agency also has attempted to design structures for a minimum of reinforcing steel. The performance of such structures has generally been good, and such deterioration as has occurred is believed related to insufficient concrete cover over reinforcing steel that permitted corrosion to occur.

The role of chlorides in seawater in chemical interaction with concrete is twofold. Chlorides act independently to do those things that chlorides are capable of doing, and they also tend to retard or inhibit the action of sulfates. The presence of chlorides, as in seawater, retards or inhibits the expansion of concrete by sulfate solutions, but not the degree of reaction. Lea (1956) cited the work of Batta, who attributed this effect to the greater solubility of gypsum and calcium aluminum sulfate in chloride solutions, and it is the reason why failure arising from chemical attack by seawater is not preceded by swelling to the same degree as in solutions of sodium or magnesium sulfate.

Griffin and Henry (1964) studied, separately, the effects of sodium chloride and seawater salts in concrete. Their purpose was to determine the effect of sea-salt spray on concrete and the permissible amounts of salt in concrete when it is mixed. They found that the optimum salinity of mixing water for maximum compressive strength was from 18 to 36 g/kg when sodium chloride was used and up to 88 g/kg when sea salt was used. They also found that, when sodium chloride was used, the rate of moisture migration through concrete from a region of higher to one of lower relative humidity decreased with increasing salinity of mixing water to a salinity of about 70 g/kg and then remained relatively constant with

further increases in salinity. When sea salt was used, the rate of moisture migration also decreased with increase in salinity, but leveled off at about 25 g/kg.

They concluded that some salt may be beneficial to concrete in some respects. With a mixing water salinity of about 25 g/kg, strength was improved, the rate of moisture movement was reduced and corrosion of mild steel in the low-strength concrete used in their investigation was negligible. With sodium chloride, the maximum corrosion of mild steel appeared to take place at a salinity of about 70 g/kg. It should perhaps be emphasized that Griffin and Henry were studying the "permissible amounts of salt" that could be tolerated; it is not, I believe, their intent to suggest that one would deliberately add salt to reinforced concrete if it could readily be avoided.

FROST ACTION

In regions where concrete in service is subjected to the action of freezing and thawing, probably the principal factor that has produced deterioration is frost action. Frost action produces deterioration when pores in the concrete, large enough to contain freezable water, become critically filled and the water freezes faster than it can be expelled from the pore. Pores that can contain freezable water are present in many aggregate particles. The originally water-filled spaces in cement paste are also pores that can contain freezable water. If deterioration due to freezing of freezable water in pores in aggregate particles is to be avoided, precautions must be taken either to avoid use of aggregate having such pore spaces or to avoid the development of critical saturation in the pore spaces. Deterioration of concrete due to freezing of freezable water in the cement paste can be avoided by providing the paste with an appropriate air-void system and by protecting the concrete from freezing until hydration of the cementitious materials has reduced the volume of freezable water in the paste to the amount than can freeze without damage.

The use of aggregate selection criteria such as those regularly employed by the major agencies in the United States, the mandatory use of air-entraining admixtures or air-entraining cements meeting the applicable requirements of current nationally established specifications for such products, and the control of concrete batching, mixing, and placing so as to ensure a proper air-void system in the hardened concrete will successfully prevent deterioration of concrete resulting from the uptake of moisture, the achievement of critical saturation in the susceptible pore space, and the subsequent internal expansion when the water freezes.

LEACHING

Concrete can deteriorate by having its soluble constituents dissolved and removed by solvents that percolate through it. The degree to which solution and removal will occur depends on the rate at which the solvents move through the concrete, the solubility of the soluble constituents, and the solvent power of the solvent. Once the solvent has dissolved all of the soluble material it can hold in solution, its

further movement through the concrete will dissolve and remove no additional material. If the solvent is saturated or nearly saturated before it enters the concrete, it will dissolve no material or a very small amount of material as it traverses the concrete. The most effective means of preventing deterioration by leaching is to ensure that the concrete has a low permeability. Powers, Copeland, and Mann (1959) showed that capillary continuity of cement pastes can be prevented and permeability consequently reduced greatly by use of low water-cement ratios and proper curing. Their data show that moist-cured cement pastes lose capillary continuity after curing periods somewhat as follows:

W/C	TIME REQUIRED
0.4	3 days
0.5	14 days
0.6	6 months
0.7	1 year

EXAMPLES OF PERFORMANCE OF REINFORCED CONCRETE IN MARITIME EXPOSURES

Wentworth-Shields (1956) described the first maritime reinforced concrete structure in Great Britain, constructed at Southampton in 1899, and noted that very few failures have occurred. The 1899 structure was a jetty consisting of a 100- by 40-ft deck on piles. In 1902, Town Quay, a reinforced concrete structure 360 by 20 by 34 ft high, was built at Southhampton. A few years later longitudinal cracks appeared above the mean-tide level along lines of reinforcement, due to rusting of steel. Repairs were made with pneumatically applied mortar. The rusting of the steel has been ascribed to the permeability of the concrete, but in the case of Town Quay electrolytic action was, if not the sole cause, a very important contributory cause. The 1899 structure, which is still in excellent condition, was made with dry, low water-cement ratic concrete; the 1902 one was made with a "rather wet" mixture.

Not only is the first maritime reinforced concrete structure built in Great Britain still in excellent condition, but most concrete structures in seawater exposures are in good condition when good practice was used and care was taken in their design and construction. For example, the concrete ship "Atlantus," the first constructed by the United States Government, was launched in 1918. It was brought to Cape May, N. J., to serve as a terminal for a ferry line and in 1927 became stranded on a sandbar. It was inspected at various times between 1918 and 1930. A report on its trial run in 1919 from Brunswick, Ga., to Charleston, S. C., states that the concrete was "in a practically perfect state of preservation with no important rust stains visible, although there could be traced in certain places on the hull the faint markings of hairline cracks which paralleled the system of reinforcing closest to the outer surface." Walter, in 1929, published a photograph of a specimen of concrete taken from the ship in 1928 showing the imprint of a square bar 13/16 in. and a round bar 5/16 in. from the outer exposed surface of the concrete, and stated that the steel was not corroded. After an examination of the ship in 1928, it was reported that a very pronounced rust stain had developed in the bulkhead enclosing the afterquarters, and in

one spot the bars parallel to the deck were clearly outlined for a space of 2 or 3 ft each way. A close inspection of this area showed that there was almost no concrete coverage. In some places the intended depth of coverage was 1/4 in.; in some cases the actual coverage was less than 1/16 in. A disc of concrete 3 in. in diameter and 0.7 in. thick was cut from a fragment collected in 1928, tested in the laboratory, and found to have very low water permeability (McMillan, 1928).

Similar inspection reports have been recorded on other concrete ships built during World War I. The "Selma," now stranded near Galveston, Texas, was inspected and reported on by Rogers at the 1953 Regional Meeting of the American Concrete Institute. The "Selma" was a tanker built in Mobile in 1918 and sunk at Galveston in about 1923. Samples of the concrete tested in 1953 showed a compressive strength of about 10,000 psi. No corrosion of steel was observed, even though less than 1 in. of cover was provided. Another of these vessels, the "Palo Alto," is exposed on the Pacific coast at Seacliff Beach State Park, 6 mi south of Santa Cruz, Calif., where it is used as a fishing pier. It was built as a tanker during World War I and is 435 ft long. It remained anchored in the Oakland Estuary, where it was built, until 1930 when the Cal-Nevada Stock Company purchased it and had it towed to Seacliff on Monterey Bay, about 100 mi to the south. The sea cocks were opened and it now rests on a sandstone shelf. It was later acquired by California when the state park was created. The ship has broken its back, but a gangway across the fracture permits both parts to be used. It is probably the most accessible of the remaining World War I concrete ships.

At the 18th Congress of the Permanent International Association of Navigation Congresses, it was "agreed that the deterioration of concrete in warm seawater is mainly due to chemical action, namely, the change in composition of the cement caused by the chlorides and sulphates present in the water. Little can be done to protect poor concrete, the remedy being to select a suitable type of cement and good sound aggregates in the first place, and to take steps to ensure that the finished product is as dense and impermeable as possible. In colder water, chemical action is less severe and the main damage is done by temperature changes. There are other causes of deterioration, such as abrasion and acids deposited by lithofagous organisms" (Warren, 1956).

CONCLUDING STATEMENT

From the foregoing discussion, it might be assumed that it is the intent of this paper to suggest that information is now available which will permit the preparation of specifications which, if followed, will preclude the occurrence of deterioration of concrete exposed to the sea. This is a proper conclusion with only relatively minor qualifications. If cost were not an important objective in preparing specifications for concrete, it would ~~certainly~~ be possible to specify concrete materials, mixtures, and construction practices which ~~, if followed,~~ would provide virtually complete assurance that deterioration of the concrete over any desired service life, at least for up to 100 years, could be avoided. In some cases, however, such a specification would require the importation of large quantities of materials from great distances and would require a degree of testing, inspection, and control that is not now

regarded as economical in concrete construction. It therefore is necessary and will continue to be necessary to take into account locally available materials and less than optimum degrees of inspection and control. This being the case, the actual specifications for most concrete for exposure to the sea will in some respects require materials and practices of less than optimum quality and the materials and practices actually obtained will, to some extent, be inferior to that which was apparently intended. In spite of these difficulties, it is believed that through use of practical specifications and practical inspection and control measures, deterioration of concrete exposed to the sea can be kept within limits so that only acceptable maintenance costs will be required. It may also be inferred that the catalog of deterioration-producing phenomena is now complete. This, of course, is something about which it would be dangerous to make a positive statement, especially since phenomena such as alkali-carbonate rock reaction have come to light only in the last few years. It is, however, believed that it is unlikely that there are major deterioration-producing phenomena, the occurrence of which is not reasonably precluded by the imposition and enforcement of current specifications.

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